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Average Molecular Weight Measurements of Some Niger Delta Crude Oil Using Vapor Pressure Osmometry and Gas Chromatography Techniques

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Abstract: The average molecular weight measurement of some selected crude oil samples around the Niger Delta region using Vapor Pressure Osmometry and Gas Chromatography have been studied. GC fingerprint spectrum for all the samples were equally obtained and revealed that all samples are of different origin. The densities @25^{o}C and API @15^{o}C values for the samples were also determined. The sample OGB-1 gave the highest API value of 53.31^{o} and density of 0.7569 (g/cm^{3}) thus of better quality than the other samples ADN-2, ADN-3, UDL-4, COY-5 with API values 17.79^{o}, 20.27^{o}, 26.84^{o}, 34.56^{o} respectively. The molecular weight value by VPO technique for all the five samples were comparatively higher than the ones given by GC. Comparing the two techniques, gave a very high correlation with R^2 value of 0.998. On the premise of density being a function of molecular weight, the two techniques had a measure of congruence. Thus, VPO and GC methods are plausible for molecular weight determination.

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1. Introduction

Crude oil characterization involves the identification of the physical and chemical properties of crude oil. This is important in estimating feedstock properties for refinery units, to produce optimal amount of finished products, to meet product quality specifications and to provide an economic assessment for crude oils (Petrotechintel.com).

Crude grades differ considerably in yield and properties. The value of any particular crude depends upon the specific product slate and refinery configuration (Petrotechintel.com). Knowing what your crude is worth begins by having good crude assay data which provides the basis for economic valuation, engineering design and refinery processing (Ghulam 2013).

One essential physical property that should be put into consideration before the completion of any crude oil characterization is the relative molecular mass. The average molecular mass of hydrocarbon is very useful when characterizing reservoir fluids and in simulation of composition (Linzhou, *et al* 2014; Ishehunwa, *et al*., 2013).

Molecular weight is a fundamental property in the characterisation of oils and its key in forecasting the composition and the worth of the oil (Riazi, 2005). Molecular weight also suggests the magnitude of a molecule and the configuration of a compound (Riazi, 2005). Molecular weight plays numerous and very vital function chiefly in areas of material and energy balance. Also, its expediency is seen in areas such as thermodynamic phase equilibrium, reaction kinetics and unit operations (Schneider, 1998). The average Molecular Weight of petroleum fractions is determined generally from any of the following three methods: Chromatographic method, Vapor Pressure Osmometry method and Cryoscopic method.

The vapor pressure osmometry (VPO) technique relies on the measurement of the difference in the vapor pressure of sample solution and vapor pressure of a pure solvent. Generally, the surface molecules of liquids tend to escape and evaporate even though the liquids are not at the point of boiling. Surface molecules that have higher energy escapes and thus evaporation occur. VPO technique gives a precise assessment compared to what is obtainable using mass spectroscopy (MS) when used for the analysis of weak or non-polar compounds such as crude oils (Yang and Eser, 1999).

For petroleum asphaltens, measuring its average molecular weight has caused quite a lot of controversies. Reasons being that asphaltens tend to associate, strongly adsorb on surfaces and are also known to be non-volatile (Wiehe, 2007; Agrawala, 2001). In defense of vapor pressure osmometry for measuring molecular weight Wiehe (2007) found that the VPO technique gives a measurement of number molecular weight average that is consistent, this trend is not seen with other analytical methods.

According to Acevedo, *et al*., (2005), VPO technique is extensively useful for the molecular weight measurement of asphaltenes and bitumen because it is uncomplicated and cost efficient. Molecular weight determination of compounds has been carried out using gas chromatographic (GC) and vapor pressure osmometry (VPO) techniques. DeCanio, *et al* (1990) determined the molecular weights of the Rattawi vacuum residuefractions and compared the mass spectrometric technique with that of vapor phase osmometry while Silva, *et al* (2011) did a comparative study on castor oil molecular weight using both GC and VPO. From their study, molecular weight determination using GC techniques gave comparatively higher values than the vapor pressure osmometry technique.

In the present study, the average molecular weight of some crude oil samples selected from different locations with-in the Niger Delta region of Nigeria will be determined using Gas Chromatography and Vapor Pressure Osmometry techniques.

2. Materials and Methods

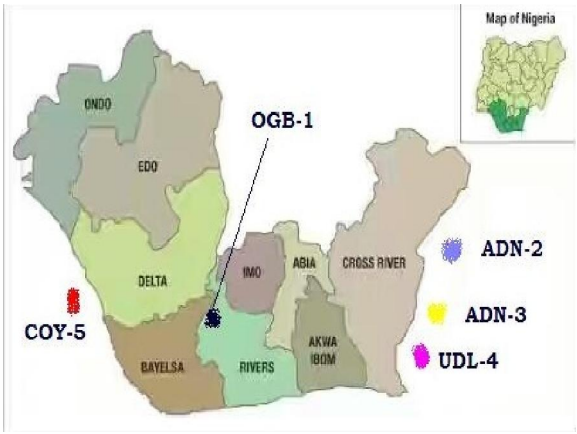
Composite crude oil samples (five) were collected at different locations within the Niger delta region (onshore and offshore). The samples were properly labeled OGB-1, AND-2, AND-3, UDL-4 and COY-5; and carefully stored for analysis. The sampling locations are as indicated in picture 1 below:

All reagents used were of analytical grade from BDH chemicals.

The density and API gravity was obtained using the DMA 4500 Density analyser. A Gas chromatograph (Star-lite Air compressor model 1120926 GC) with an FID (flame ionization detector) was the device used for the compositional analysis.

The Knauer Vapor Pressure Osmometer (VPO) instrument model K-1000 was used for Vapor pressure osmometry measurements in accordance with Knauer Guide of VPO (2007). Here, Naphthalene was used as the reference standard, and benzene was the solvent. Different concentrations of Naphthalene in benzene solution and the crude oil samples in benzene were prepared, after which the Osmometry analysis of the solutions were determined according to its standard operating procedure. The measurements were done in triplicates and the average taken. Two curves were generated for the reference standard data and crude oil data. The first one is the graph of the osmometer reading on Y-axis was plotted against the weight % of the standard of the on the X-axis to obtain the reference standard slope. The second is a graph of the osmometer reading on Y-axis was plotted against the weight % of the crude oil samples on the X-axis to obtain the crude oil samples slope. The Molecular weight (Mw) was determined by the relationship below:

$$Mw\left(\frac{g}{mol}\right) = \frac{Calibration\ slope \times Mw\ of\ Naphthalene\left(128.1705\frac{g}{mol}\right)}{Sample\ slope} \quad \ldots 1$$



Picture 1: Map of Niger-delta of Nigeria showing the sampling locations

3. Results

The average molecular weights obtained using the two techniques (VPO and GC), their respective API gravities and densities are presented in Table 1. A bar chart comparing the average molecular weight obtained by the two methods from the various points of sampling is equally shown in Figure 1. On the other hand, Figure 2 shows the graphical correlation of average molecular weights by gas chromatography and vapor pressure osmometry. The plots correlating density and molecular weights by VPO and GC are presented in figures 3 and 4 respectively. Figure 5 presents plots of osmometry reading versus concentration in weight%, while the fingerprints spectrum for GC analysis of the crude oil samples are described in Figures 6 - 10.

Table 1. Densities, API gravities and Molecular weights of Crude Oil Samples from OGB-1, ADN-2, ADN-3, UDL-4, and COY-5 Wells

Sample Id	Density@ 25°C (g / cm^3)	API @ 15°C	Mol. Wt. by Gas Chromatography (g / mol)	Mol. Wt. by Vapor Pressure Osmometry (g/mol)
OGB-1	0.7569	53.31	122.065	124.910
ADN-2	0.9405	17.79	214.262	215.230
ADN-3	0.9249	20.27	205.099	210.770
UDL-4	0.8859	26.84	185.660	187.599
COY-5	0.8441	34.56	158.626	162.080

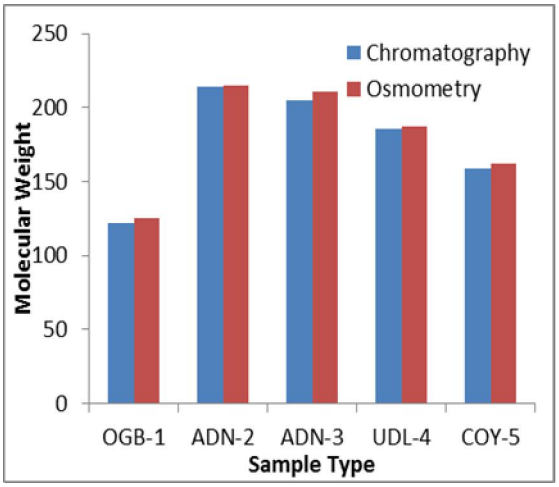


Figure 1. Bar Chart showing Molecular weight by Gas Chromatography and Osmometry

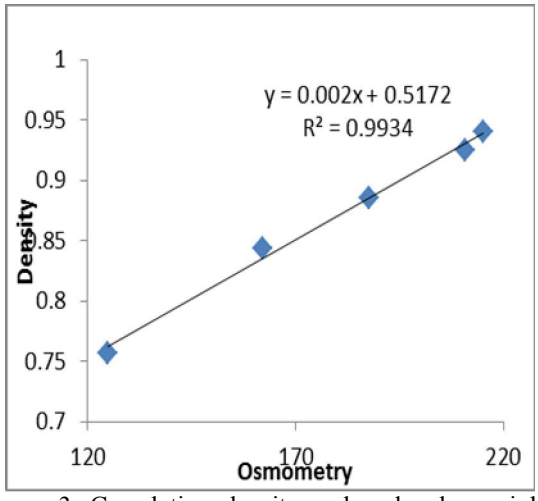


Figure 3. Correlating density and molecular weights by VPO

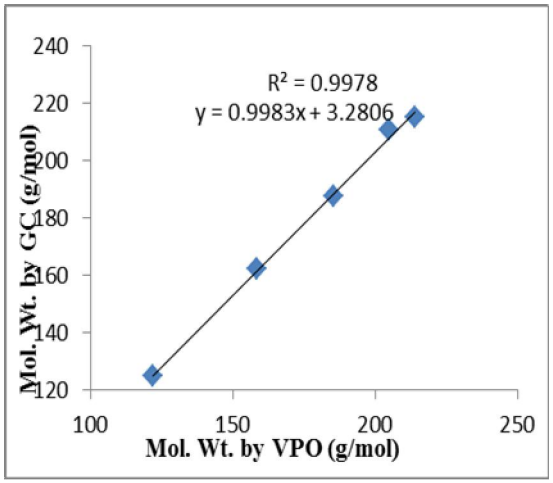


Figure 2. Graphical Correlation of Molecular weights by Gas Chromatography and Osmometry

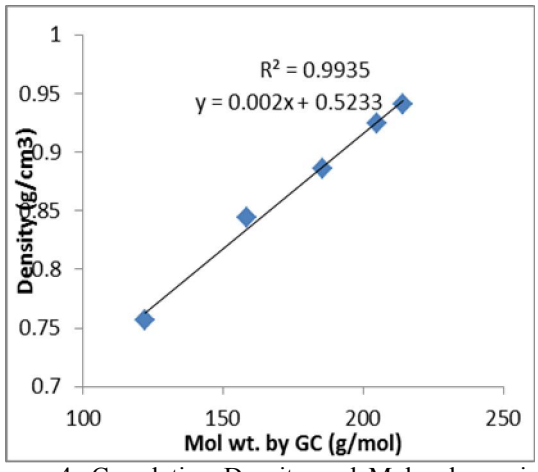


Figure 4. Correlating Density and Molecular weight by GC

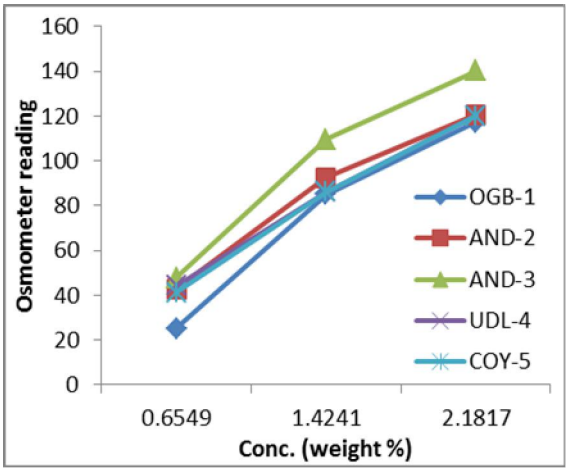


Figure 5. Plots of osmometry reading versus concentration in weight%

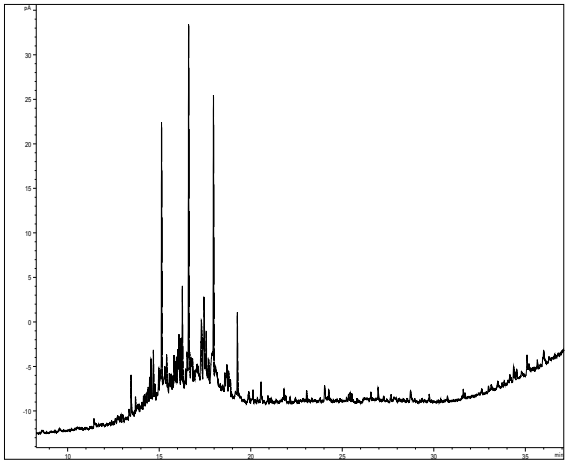


Figure 8. Fingerprint chromatogram for sample ADN-3

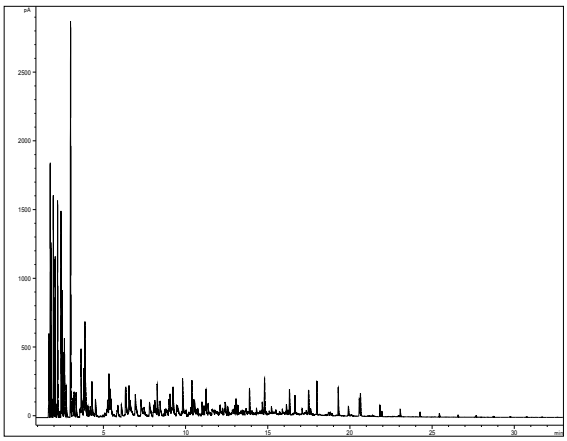


Figure 6. Fingerprint chromatogram for sample OGB-1

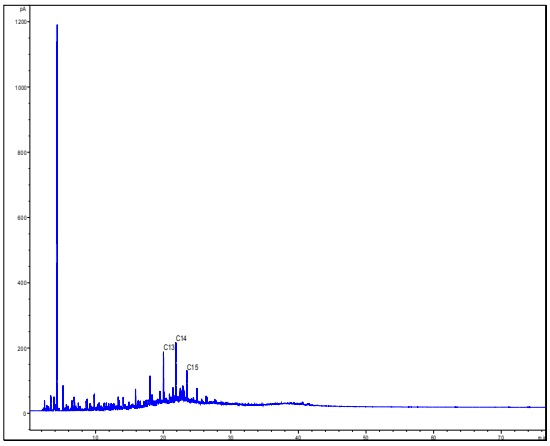


Figure 9: Fingerprint chromatogram for sample UDL-4

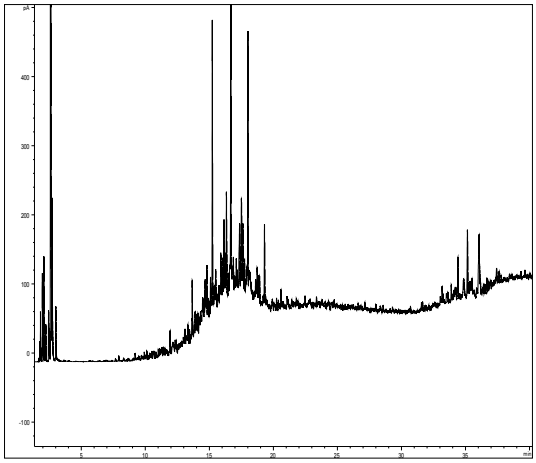


Figure 7: Fingerprint chromatogram for sample ADN-2

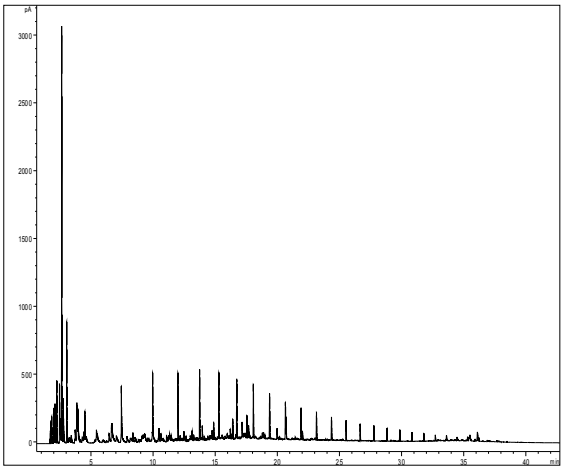


Figure 10: Fingerprint chromatogram for sample COY-5

4. Discussion

Results obtained from table 1 shows that the density of the crude oil samples analysed ranged from 0.7569 (g/cm^3) - 0.9405 (g/cm^3), and their API values ranged from 17.79^0 to 53.31^0. According to Ghulam, *et. al.*, (2013), the classification of crude oil is as light, medium or heavy, based on its measured API gravity. Light crude is any crude oil having an API value higher than 31.1°API. Medium oil is defined as oil that is having API gravity between 22.3°API and 31.1°API, while heavy crude oil is defined as one that has API gravity less than 22.3°API (Daubert and Danner, 1997; Schneider, 1998). Similar classifications have also been documented by Lousiana Department of Natural resources, (1989).

Thus from our study, OGB-1 and COY-5 samples with densities of 0.7569 (g/cm^3) and 0.8441 (g/cm^3), and API values of 53.31°and 34.56° respectively, indicates that the crude oil samples can be classified to be light. UDL-4 sample with density of 0.8859 g/cm^3 and API of 26.84° falls in the medium crude category while the ADN-2 and ADN-3 crude samples having densities of 0.9405 (g/cm^3) and 0.9249 (g/cm^3), and API gravities of 17.79° and 20.27° respectively suggests they are heavy crude. Thus we have two light crudes (OGB-1 and COY-5), one medium (UDL-4) and 2 heavy crudes (ADN-2 and ADN-3).

Specific gravity of crude oil gives a rough measure of the quantity of lighter hydrocarbons present (Ghulam *et al.,* 2013). The lower the value of the specific gravity (which is a function of density) and higher the API gravity, the higher is the yield of light fractions by distillation (Riazi, 2005, Riazi and Al-Sahhaf 1995). According to Ghulam, *et al.*, (2013), any crude oil with higher API gravity tends to have a higher price and is of good quality. This implies that crude oil sample collected from OGB-1 is of better quality and invariably of higher market price than the crude oil samples obtained from ADN-2, ADN-3, UDL-4, COY-5.

Based on the experimental objective of determining average molecular weight of crude hydrocarbon oil samples, figure 1 clearly reveals that GC and VPO techniques are plausible for determining molecular weights. Sample ADN-2 with molecular weight of 214.262 g/mol by GC and 215.230 g/mol by VPO gave the leading value. This was followed by sample ADN-3 and UDL-4 with molecular weight of 205.099 g/mol by GC; 210.770 g/mol by VPO and 185.660 g/mol by GC; 187.599 g/mol by VPO respectively while sample COY-5 with molecular weight of 158.626 g/mol by GC and 162.080 g/mol by VPO was next. Sample OGB-1 with 122.065 g/mol by GC and 124.910 g/mol by VPO had the smallest value. From the results so far, sample ADN-2 tends to be the heaviest while sample OGB-1, the lightest. However, VPO technique gave relatively higher values for average molecular weight determination than results obtained with GC technique. This corresponds to what was reported by Silva, *et al.,* (2011) in their study on castor oil molecular weight by VPO and GC which gave values of 928.88g/mol and 928.30g/mol respectively. Furthermore, graphical correlation of molecular weights by gas chromatography and vapor pressure osmometry indicates an R^2 value of 0.993 (close to 1) for both VPO and GC with a constant correction factor of 3.280 as presented in figure 3 and 4.

Additionally, figures 3 and 4 which describes the plots that correlates the molecular weights by the two techniques (VPO and GC) and their densities reveals that the data can be modelled by a straight line fit. From the plots, we observed that density increased with an increasing molecular weight, which shows that density is directly related to molecular weight (Riazi, 2005).

Also, it further corroborate with the equation of state in which:

$$PV = nRT \ldots\ldots\ldots 2$$

Where n = number of moles and can be expressed as mass/molar mass.

Then, $density = mass/volume \ldots\ldots\ldots 3$

From equation (3), $mass(m) = density\ (\rho) X\ volume\ (V) \ldots\ldots\ldots 4$

$$Number\ of\ moles\ (n) = {mass\ (m)}/{Molar\ mass\ (MM)} \ldots\ldots\ldots 5$$

Substituting (5) in (2) we have,

$$Pv = {mRT}/{M.M} \ldots\ldots\ldots 6$$

Thus, $M.MPv = mRT$

Putting (4) in (6) we get; $M.MPv = \rho VRT$

$$M.MP = \rho RT \ldots\ldots\ldots 7$$

From equation (7) we see the direct proportional relationship between M.M (Molecular mass or weight) and the density (ρ).

Also, carefully looking at the graphical representation of all the five samples analysed for VPO in figures 5 revealed that the osmometer reading increases with increase in solution concentration in weight %. The straight line shows proportionality between the measured value and the concentration (Silva, *et al*., 2011). This corroborates the theoretical assertion that states that vapor pressure is a colligative property and its lowering is a function of the number of solute particles per the number of solvent molecules in solution (McQuarrie, *et al*., 2011).

Finally, figures 6 to 10 presents the fingerprint gas chromatogram for the five samples (OGB-1, ADN-2, ADN-3, UDL-4, COY-5) respectively. The fingerprints of all the samples are distinctly different from one another and indication that all five crude oil samples originates from different source and thus unique.

5. Conclusion

From the study, results obtained show that the densities and the API gravities of the crude oil samples indicates two of the crude oil samples OGB-1 and COY-5 as light crude oil, UDL-4 as medium crude oil, while samples ADN-2 and ADN-3 as heavy crude oil. The sample OGB-1 gave the highest API value of 53.31^{o} and thus of better quality than the other samples ADN-2, ADN-3, UDL-4, COY-5 with API values 17.79^{o}, 20.27^{o}, 26.84^{o}, 34.56^{o} respectively and invariably of higher market price.

The molecular weight value by VPO technique for all the five samples were comparatively higher than the ones given by GC. Since the research of Silva *et al*., (2011) showed that VPO presents a more accurate result for molecular measurement, it can therefore be said that molecular weight obtained by VPO could be more reliable than the ones obtained by GC. The weights were estimated within the limits of experimental errors. Comparing the two techniques, there is a correlation between them. On the premise of density being a function of molecular weight, the two techniques had a measure of congruence.

The VPO plots for the analysed samples shows that the osmometer reading increases as the solution concentration also increases. The vapor pressure of a solution reduces as the number of solute particles increases (Riazi, 2005).

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